Abstracts

Abstracts

Tree species of excavated wooden relics from Terada site (Heian era), S. HAHASHI: Kitakyuushu Maizou Bunkazai Chousa Houkoku (Examination Report of Excavated Treasures of Terada Site) No. 70, Chap. IV, Natural Scientific Analysis, 103-107, Pl. 1-4, Kitakyuushuu City, Educational and Cultural Committee (1988) (in Japanese)

Excavated 47 wooden relics were identified, and 27 specimens were coniferous species and 20 were broad leaved tree species. In conifer, 18 samples were identified to *Cryptomeria japonica* D. Don, and 6 samples among these were used for well-tube. Other coniferous species were as follows; *Torreya nucifera* Sieb. et Zucc., *Podocarpus macrophyllus* Lamb., *Pinus* spp. (Diploxylon) and *Chamaecyparis obtusa* Endl. In broad leaved tree, *Cinnamomum camphora* Sieb. (6 specimens), *Quercus* spp. (Cyclobalanopsis 4), *Eurya japonica* Thunb. (4), *Castanea crenata* Sieb. et Zucc., *Deutzia crenata* Sieb. et Zucc., *Distylium racemosum* Sieb. et Zucc. and *Cleyera japonica* Thunb. The half of *C. camphora* were used for well-tube.

Tree species of excavated wooden relics from Furudono site (Kofun era), K. SHIMAJI and S. HAYASHI: Kyoto-fu Iseki Chousa Houkoku (Kyoto Prefecture, Examination Report of Sites) No. 9, Furudono Site, 98-105, Kyoto Pref., Examination and Research Center of Excavated Treasure (1988) (in Japanese)

Excavated 158 wooden relics werw identified. *Cryptomeria japonica* D. Don were main species (75 specimens) of sivil engineering and archtectural works (94), and 58 specimens of living materials (62). Other 2 samples were arms and one was identified *C. japonica*. *C. japonica* occupied very high 84.8%, and this is the remarkable feature in this site.

Identification of excavated charcoal from Kokanda site (5th Cent.), K. SHIMAJI, S. FUKUDA and S. HAYASHI: Sakai-si Bunkazai Chousa Houkoku (Sakai City, Examination Report of Treasures) No. 33, Kokanda Site, Chap. 5, Natural Scientific Analysis of Site, Sect. 1, 174-175 (1988) (in Japanese)

Specimens of charcoal were collected from Sueki kiln. All specimens were identified to *Quercus acutissima* Carr.

Tree species of wooden implements excavated from Fukae-kitamachi site (Nara era), K. SHIMAJI and S. HAYASHI: Fukae-Kitamachi Iseki, Hyougo-ken Bunkazai Chousa Houkoku (Fukae-Kitamachi Site, Hyougo Pref., Examination Report of Treasures) No. 54, Chap. 3, Sect. 8, 109-111, Hyougo Pref., Educational Committii (1988) (in Japanese)

Excavated 11 wooden implements were identified. Tageta (paddy field clog, 3 specimens), Tsuchinoko (wooden weight for making straw mat, 2), Igushi (ceremonial boundary marker, 4) and bottom of Magemono (round chip box, container made from bent slat of wood, 1) were all identified to *Chamaecyparis obtusa* Endl. Sou (container made by hand, wooden basin, 1) was identified *C. obtusa* or *Cryptomaria japonica* D. Don. Tree species of Igushi, *C. obtusa*, was same with excavated from other site, but Tsuchinoko, *C. obtusa*, was very rare because it is not so heavy.

Tree species of clog excavated from Hase Kaizuka (Shell-mound) (Latter half of Jomon era), K. SHIMAJI and S. HAYASHI: Hyougo-ken Bunkazai Chousa Houkoku (Hyougo Pref., Examination Report of Treasures), No. 61, Hase Kaizuka, 30, Pl.9, Hyougo-ken Kyouiku Iinkai (Hyogo Pref., Educational Committii) (1988) (in Japanese)

Identified tree species of this clog was *Cryptomeria japonica* D. Don.

Tree species of wooden well, N. ISOGAWA, K. HAMAZAKI and T. ITOH: A report of investigation for the excavation of Kyoto University Campus in 1986, Part I, 5-53 (1989) (In Japanese)

29 wood specimens collected from 13 wooden well excavated from the site of AJ18 and AJ19 in the campus of Kyoto University Hospital was examined microscopically. 18 of them were identified as *Chamaecyparis obtusa;* 9 as *Cryptomeria japonica,* 1 as *Abies firma,* and 1 as *Sciadopitys verticillata* .

Wood species excavated from the site of Muromi river in 23rd investigation of Shika relics, T. Itoh: In "a report of 23rd investigation of Shika relics in Fukuoka city", A report of investigation for buried cultural properties in Fukuoka city, No. 196, 35-38, PL17-PL20, the board of education in Fukuoka city, (1989) (in Japanese)

38 wooden specimens excavated from the Shika relics which covers from BC 200 to AD 600 were examined microscopically. Those collected from 25 different posts were identified as *Cephalotaxus harringtonia* f. *drupacea, Castanea crenata, Castanopsis sp., Quercus sp.* (Cyclobalanopsis), *Quercus sp.* (Lepidobalanus), *Persea thunbergii, Ilex sp , Pittosporum tobira, Myrsine seguinii, Camellia japonica, Cleyera japonica, Eurya japonica, Distylium racemosum,* and *Meliosma myriantha.* Those from 7 different wooden boards were identified as *Castanea crenata, Castanopsis sp., Quercus sp.* (Cyclobalanospis), and *Quercus sp.* (Lepidobalanus). Three farming tools so called "Eburi" and "Kuwa" in Japanese were identified as *Quercus sp* (Cyclobalanopsis). The only one spatula was identified as *Cephalotaxus harringtonia* f. *drupacea* .

Lectin from the trunk of *Sophora japonica*, K. BABA and H. KURODA: Wood Sci. Technol. **23**, 171-178 (1989)

Lectin was purified from the bark of *Sophora japonica* trunk by a simple method, affinity chromatography on acid-treated agarose; the yield was about 27% of the total sap protein. Its molecular weight was 135,000±5,000 shown by using gel filtration, similar to that of the seed lectin of this species. When analyzed by using polyacrylamide gel electrophoresis (PAGE) under acidic and basic conditions, the lectin showed multiple bands. These patterns were different from those obtained with the seed lectin of the same tree. The trunk lectin had a broader specificity for the blood types than the seed lectin. These observations demonstrate that the trunk and the seed lectins from the same tree are different molecular species.

Evidence for an ester linkage between lignin and glucuronic acid in lignin-carbohydrate complexes by DDQ-oxidation, T. WATANABE and T. KOSHIJIMA: Agric. Biol. Chem., **52**, 2953-2955 (1988)

Direct evidence for the existence of ester linkages between lignin and 4-*O*-methylglucuronic acid residue in wood hemicelluloses was obtained by a new method using a diazomethane-methylation and subsequent oxidative cleavage of substituted benzyl glucuronate with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). A DDQ-treat ment of a diazomethane-methylated LCC fraction from *pinus densiflora* wood showed formation of free carboxyl groups of 4-*O*-methyl glucuronic acid residues. Because methyl glucuronate could not be decomposed by DDQ but the ester linkages between glucuronic acid residue and 3,4-disubstituted lignin units were cleaved by DDQ, it is concluded that lignin is directly bound to the hemiculluloses through a carboxyl group of the glucuronic acid residue in *Pinus densiflora* wood.

Application of APT pulse sequencce to facilitate ^{13}C-NMR analysis of lignin, T. WATANABE and T. KOSHIJIMA: Wood Res., No. 75, 13-20 (1988).

A convenient J-modulation pulse sequence, Attached Proton Test (APT) technique has been applied to the acetylated milled wood lignin from akamatsu wood. Signals originating from *p*-acetylated guaiacyl nuclei were estimated by comparing two types of acetylated milled wood lignin, that is, *p*-methylated (MWLma) and *p*-acetylated (MWLa) preparations from the softwood. Reaction of diazomethane with cinnamaldehydes in the lignin was confirmed from the APT spectra of both acetylated fractions.

Structural features of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone-oxidized lignin acetate revealed by carbon-13 nuclear magnetic resonance spectroscopy,

T. WATANABE and T. KOSHIJIMA, Mokuzai Gakkaishi, **35**, 130–134 (1989).

Acetylated milled wood lignin (MWLa) from akamatsu (*Pinus densiflora* Sieb. et Zucc.) wood was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Carbon-13 nuclear magnetic resonance spectra of the lignin revealed that carbon atoms at α and conjugated γ positions in guaiacylalkane units were oxidized to carbonyl groups. The spectra also provide unequivocal evidence for the oxidative cleavage of benzyl ether linkages by the action of DDQ.

Binding-site analysis of the ether linkages between lignin and hemicelluloses in lignin-carbohydrate comppexes by DDQ-oxidation, T. WATANABE, J. OHNISHI, Y. YAMASAKI, S. KAIZU and T. KOSHIJIMA, Agric. Biol. Chem., **53**, 2233–2252 (1989).

Lignin-carbohydrate complexes isolated from normal and compression wood of *Pinus densiflora,* were hydrolyzed with two types of cellulase preparations and the hydrolyzates formed were fractionated by adsorption chromatography on polyvinyl gel into water-soluble materials and LCC fragments. To elucidate the binding-sites between lignin and carbohydrate, the cellulase-degraded LCC fragments were sub-jected to acetylation and then oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which was confirmed to oxidatively cleave the benzyl ether linkages between the lignin and carbohydrate. The DDQ-oxidized fraction was then methylated by the method of Prehm, hydrolyzed, reduced and acetylated. In this experiment, stabliities of acetyl group during the DDQ-oxidation and Prehm methylation were confirmed using partially acetylated glucose derivatives. GC-MS analysis of the methylated sugar from the pine LCCs revealed that alditol acetates from 6-*O*-methyl mannose, 6-*O*-methyl galactose, 6-*O*-methyl glucose and a small amount of their 2-*O*- or 3-*O*-methyl isomers existed in both methylated fractions. 2-*O*-methyl xylose and 3-*O*-methyl xylose were also detected in the fraction from the acidic LCC. These results lead to the conclusion that acetyl glucomannan and β 1,4-galactan were preferably bound to the lignin through their primary hydroxyl groups, while arabinoglucuronoxylan was linked to the lignin through C-2 and C-3 positions of the xylan main chain.

Formation of lignin-carbohydrate complex polymer and connection points among sugar chains and lignin macromolecules, T. KOSHIJIMA, J. OHNISHI and T. WATANABE, Proceedings of International Symp. on Wood and Pulping Chem. 623–627 (1989)

Frequencies and binding sites of lignin-sugar residues in native lignin-carbo hydrate complexes (LCC) which had been previously determined by us were compared with those in synthetic LCC models namely dehydrogenative polymerezation

products of coniferyl alcohol synthisized in the presence of hemicelluloses. As a result, it was confirmed that C-6 of mannose and C-3 of xylose residues were participating into benzyl-ether bonding of sugar-lignin with very high frequency. This fact would give strong support for the consideration that LCC is formed during lignin biosynthesis proceeding under occurrence of hemicelluloses.

Structure and properties of the lignin-carbohydrate complex polymer as an amplipathic substance, T. KOSHIJIMA, T. WATANABE and F. YAKU: ACS Symposium Series 397 "LIGNIN——Properties and Materials——", 11-28, (1989) The American Chemical Society, U.S.A.

It has been found that lignin-carbohydrate complexes (LCC's) consist of sugar chains and relatively small lignin fragments attached as pendant side shains; they have number-average molecular weights of ca. 6000-8000. The linkage between sugar and lignin was determined to be mainly of the benzyl ether type by a newly developed method using DDQ oxidation. Some of the LCC's exhibit a strong tendency to form micelles or aggregates in aqueous solution due to hydrophobic and also electrostatic interactions.

Ester linkages between lignin and glucuronoxylan in a lignin-carbohydrate complex from beech (*Fagus crenata*) wood, N. TAKAHASHI and T. KOSHIJIMA, Wood Sci. Technol., **22**, 231-241 (1988).

A water-soluble lignin-carbohydrate complex (LCC) isolated from beech (*Fagus crenata*) MWL was invistigated. Results from gel filtration chromatography and the infrared spectrum of the LCC treated with alkali under mild conditions indicated that the LCC contained alkali-labile bonds. Decrease of uronic acid content and the detection of 4-*O* methyl-glucose in the sodium borohydride-reduced LCC suggested the presence of an ester linkage between lignin and glucuronic acid in the glucuronoxylan. Conductometric titration also indicated the existence of glucuronic ester linked to lignin. From these results, it is concluded that the LCC contained an ester linkage between lignin and glucuronoxylan and that about one-third of the glucuronic acid present in the LCC was involved in this ester linkage.

Chemical structure of highly purified acetylglucomannan isolated from akamatsu Björkman lignin-carbohydrate complex, R. TANAKA, F. YAKU and T. KOSHIJIMA, Mokuzai Gakkaishi, **34**, 959-963 (1988).

Acetylglucomannan isolated from akamatsu (*Pinus densiflora* S. and Z.) Björkman lignin-carbohydrate complex was highly purified by the method of iodine complex formation. Linkage analysis of this acetylglucomannan by using methyla-

tion, Smith degradation, and reducing end analysis indicated that galactose residues were combined with the 1→4 linked glucomannan main chain through a 1→6 linkage. It has been manifested so far whether galactose is one of the component sugar of softwood glucomannan or an impurity coming from galactoglucomannan or mannogalactan.

From the present results, it became evident that galactose was surely a member of the component sugars of the glucomannan and existed in a molar ratio of mannose: glucose: galactose, 37:10:1.

"**Kirk-Othmer Concise Encyclopedia of Chemical Technology**" (Ed. J. Shiokawa), E. MAEKAWA transd. a part of the words, Maruzen, 1988, p. 1509.

The concise encyclopedia includes more than 750 of important terminology in chemical technology. Some related words in this encyclopedia were translated in Japanese and given an explanation.

Structural Studies of a Polysaccharide (S-194) elaborated by Alcaligenes ATCC31961 Per-E. JANSSON, B. LINDBERG, J. LINDBERG and E. MAEKAWA: Carbohydrate Res., **156**, 157–163 (1986)

The structure of the polysaccharide (S-194) elaborated by *Alcaligens* ATCC 31961 has been investigated by using the main techniques of methylation analysis, specific degradation, and ^{1}H-and ^{13}C-n.m.r. spectroscopy. As a result, it is concluded that the polysaccharide is composed of hexasaccharide repeating units containing such structure as:

$$\begin{array}{l}\rightarrow 3)\text{-}\beta\text{-D-Glc}_p\text{-}(1\rightarrow 4)\text{-}\beta\text{-D-Glc}_p\text{A-}(1\rightarrow 4)\text{-}\beta\text{-D-Glc}_p\text{-}(1\rightarrow 4)\text{-}\alpha\text{-L-Rha}_p\text{-}(1\rightarrow \beta\text{-D-Glc}_p \\ \qquad\quad 6 \\ \qquad\quad \uparrow \\ \qquad\quad 1 \\ \text{-}(1\text{-}6)\text{-}\alpha\text{-D-Glc}_p\end{array}$$

The polysaccharide further contains approximately one O-acetyl group per repeating unit, distributed over secondary positions.

A combened electron and X-ray diffraction study of cellulose tripropionate., Y. SHUTO, K. OKAMURA, J. AZUMA, F. TANAKA and H. CHANZY: J. Appl. Polym. Sci., Appl. Poly. Simp., **37**, 207 (1989)

The crystal and molecular structure of cellulose tripropionate has been determined through combined electron and X-ray diffraction analysis, aided by stereochemical model refinement. Lamera single crystals of cellulose tripropionate were prepared at 205°C in a mixture of dibenzyl ether and *n*-tetradecane. The lath shape crystal gave well-resolved electron differactograms from which the reciprocal parameters $a^*=0.91\,nm^{-1}$, $b^*=0.65\,nm^{-1}$ and $\gamma^*=90°$ could be determined. Com-

bining the electron diffraction data with X-ray diffraction data of the oriented cellulose tripropionate film, a monoclinic unit cell parameters with dimensions a= 1.176 nm, b=1.531 nm, c (fiber axis) =1.514 nm and β=106.0° were deduced. The crystal symmetry is $P2_1$ with b as unique axis. These data, coupled with the observed density of the crystals, indicate that the unit cell contains two antiparallel cellulose tripropionate chains of three residues each. The conformation of the molecule is less extended than those of cellulose triacetate or cellulose tributyrate, with successive glucopyranose residues in a threefold screw relationship. The structure solution was achieved using X-ray diffraction intensity data, with final residuals R=0.327 and R"=0.307.

Structure of a poly[(1,4)-α-D-galactosamine anhydride] studied by X-ray diffraction coupled with conformational analysis, K. OGAWA, F. TANAKA, J. TAMURA, K. KADOWAKI and K. OKAMURA: Macromolecules, **20**, 1172-1174 (1987).

X-ray fiber diffraction study coupled with an energy calculation on poly[(1,4) -α-D-galactosamine] was reported. This is the second polysaccharide having a galactopyranosyl backbone studied by X-ray diffraction. A twofold helical structure was found for the poly [galactosamine].

Conformational difference between chitosan and poly-(1,4)-α-D-galactosamine, K. OGAWA, F. TANAKA and K. OKAMURA: Proceeding of the 4th International Conference on Chitin and Chitosan, 1988.

Conformational difference between (1,4)-linked polysaccharides of α-and β-anomers of D-glucosamine and D-galactosamine was examined. X-ray diffraction measurements on fiber diagrams coupled with energy calculations of chitosan and (1,4)-α-D-galactosamine revealed that both polysaccharides take ribbon-like twofold helixes but that the former has an extended, and the latter somewhat kinked structures. In contrast, conformational analysis of (1,4)-linked polymers of α-D-glucosamine and β-D-galactosamine predicted that they take wide helixes.

Molecular and crystal structure of cellulose tripropionate (in Japanese), Y. SHUTO, J. AZUMA, K. OKAMURA, F. TANAKA and J. SUGIYAMA: Proceedings of the Symposium on cellulose, the Society of Fiber Science and Technology, Japan, 1988.

Although the crystals of cellulose are classified into four kinds of polymorph. Most of the molecular conformations of cellulose are with two-fold helical symmetry. Their polymorphs are induced only by the differences of the packing conditions of cellulose molecules.

The chains of cellulose tri-acetate, butyrate and valerate were observed to have two-fold screw axes. However, it was found that the chain of cellulose tri-propionate had three-fold screw axis. This was discussed based with its X-ray fiber diagrams and electron diffractograms.

The configurational differences between chitosan and poly[(1,4)-α-D-galactosamine] (in Japanese), K. OGAWA, F. TANAKA and K. OKAMURA: Proceedings of the 3rd Symposium on Chitin, Chitosan and their concerned Enzymes, 1988.

The configurational differences between D-glucosamine and D-galactosamine come from the positions of the oxygen atom on the fourth carbon atom. The conformations of their molecules are, therefore, expected to be remarkably different, when the chains contain (1,4)-linked glycosidic linkages. However, similar characteristics of solution were detected between poly[(1,4)-β-D-glucosamine] and poly [(1,4)-α-D-galactosamine], although their configurations of oxygen atom on the fourth carbon atom were different. This was discussed based on their conformations.

Roles of secondary metabolism of wood rotting fungi in biodegradation of lignocellulosic materials, M. SHIMADA, A. OHTA, H. KUROSAKA, T. HATTORI, T. HIGUCHI and M. TAKAHASHI: in, "Plant Cell Wall Polymers" (Eds., N.G. Lewise and M.G. Paice) ACS Symposium Series **399**, 412-425 (1989).

The brown-rot fungus *Lentinus lepideus* was found to produce 5 different phenylpropanoids and methyl p-anisate as the secondary metabolites in high and low nitrogen cultures. A new metabolite, p-methoxyphenyl propyl alcohol was also detarmined. The white-rot fungus *Phanerochaete chrysosporium* produces veratrylglycerol and veratryl alcohol as the secondary metabolite in the extracellular culture fraction. "Ligninase" of this white-rot fungus was found to catalyze Cα-Cβ cleavage of veratrylglycerol, yielding glycolaldehyde and veratraldehyde. Both a synthetic lignin model substrate and the natural metabolites of the white-rot fungus were oxidized by the same extracellular peroxidase.

The possible roles of the nitrogen recycling system and cinnamate pathway which are involved in the secondary metabolism of L-phenylalanine in brown-rot and white-rot fungi are discussed in relation to the wood decay processes.

Lignin peroxidase and the biomimetic catalysts, M. SHIMADA: Chemistry and Biology, **27**, 419-421 (1989) (in Japanese)

Current topics of lignin biodegradation with lignin peroxidases and its biomimetic catalyst were briefly described. A new biomimetic system developed with

Mn/Co/peracetic acid in our laboratory in order to bleach kraft pulps was also introduced.

Lignin biodegradation, M. SHIMADA: in, "Lignin Utilization", (Eds., E. Sada and H. Asaoka), Japan Tappi **43**, 22-23 (1989) (in Japanese).

Recent advances in lignin biodegradation research with microbial, enzymatic and biomimetic systems are briefly reviewed.

Chemical degradation methods for characterization of lignins, M. TANAHASHI, and T. HIGUCHI: "Methods in Enzymology, Vol. **161**, Biomass Part B, Lignin, Pectin, and Chitin" (Eds., W.A. Wood and S.T. Kellogg), Academic Press, Inc., San Diego, pp. 101-109 (1988)

Acidolysis, thioacidolysis, alkaline nitrobenzene oxidation, and permanganate oxidation have been mainly adopted for characterization of chemical structure of lignin. The procedures of these chemical degradation mathods were expounded in detail.

Degradation mechanism of lignin by steam explosion I. Degradation products of lignin and β-O-4 lignin substructure model dimers, M. TANAHASHI, M. KARINA, K. TAMABUCHI and T. HIGUCHI: Mokuzai Gakkaishi, **35**, 135-143 (1989)

The ether soluble fraction of steam-exploded wood lignin of white birch (*Betula platiphilla* Sukatchev var. *japonica* Hara) mainly contained d,l-syringaresinol, d,l-epi-syringaresinol, dehydrodiconiferyl alcohol, coniferaldehyde, synapaldehyde, coniferyl alcohol, sinapyl alcohol, vanillin, syringaldehyde, vanillic acid, syringic acid, furfural, 5-hydroxymethylfurfural, and betulin.

By steam explosion, guaiacylglycerol- and syringylglycerol-β-guaiacyl ethers gave coniferyl and sinapyl alcohols, respectively, as main products with small amounts of dehydrodiconiferyl alcohol and syringaresinol, respectively. The results suggested that the β-O-4 ether linkage of the substrates mainly was cleaved homolytically to produce cinnamyl alcohol radicals which are converted to cinnamyl alcohol and their dimers.

Hence, we propose a radical reaction as the main degradation mechanism of lignin by steam explosion.

Characterization of Steam-Exploded Wood III. Transformation of cellulose crystals and changes of crystallinity, M. TANAHASHI, T. GOTO, F. HORII and T. HIGUCHI: Mokuzai Gakkaishi, **35**, 654-662 (1989)

Chemical changes of cellulose by steam-explosion were examined by X-ray diffraction, electron microscopy and CP-MAS ^{13}C-NMR spectroscopy. By steam-

explosion (28 kgf/cm^2, 230°C, 16 min.) cellulose in white birch wood was increased in crystallinity (CrI: 51% to 63%), micelle width (25 Å to 43 Å) and microfibril width (32 Å to 44 Å), whereas the length of cellulose microfibril was decreased (to about 2000 Å). The crystalline form of cellulose was clearly changed by steam-explosion: Broad peaks in CP/MAS ^{13}C-NMR spectrum of crystalline component of wood cellulose assigned at C_1, C_4 and C_6 of pyranose ring changed to the spectrum of fine doublet peaks of crystal form, cellulose Ia. It was also found that crystallinity of cellulose is increased by steaming of wood at high temperature and high steam pressure without explosion. However, purified high crystalline cellulose such as filter paper was less influenced in crystallinity by steaming, and the results suggested that other constituents accompanying cellulose were involved in the increase of crystallinity of cellulose by steam-explosion.

Reaction of main components of wood by steaming and steam explosion, M. TANAHASHI: Report of the sectional researching committee meetings of Japan Mokuzai Gakkai, pp. 377–380 (1989) (in Japanese)

Characterization and reaction mechanism of main components of steam-exploded or steaming wood were expounded for the total utilization of woody biomass.

Utilization of lignin……Physiological activities of steam-exploded lignin and separation of chemicals from lignin, M. TANAHASHI: Report of the sectional researching committee meetings of Japan Mokuzai Gakkai, pp. 408–410 (1989) (in Japanese)

Physiological activities (e.g. desmutagenity) of steam-exploded lignin were described and separation of chemicals (e.g. syringaresionol) from lignin was explained as an interesting research for the utilization of exploded lignin.

Utilization of cellulose, M. TANAHASHI: Report of the sectional researching committee meetings of Japan Mokuzai Gakkai, pp. 411–415 (1989) (in Japanise)

Recent utilization of cellulose was described about the structure, physical properties, separation and purification method and utilities as functional celluloses.

Separation and effective utilization of wood components by steam explosion, M. TANAHASHI: in "**Effective Utilization of Lignin**" (Eds., E. Sada and H. Asaoka), Japan Tappi J., **43**, 754–757 (1989) (in Japanese)

Steam explosion process of lignin, which is a practical process utilizing decomposition reaction of ether linkages is outlined and reactions and separations of derived components are explained to search for a possibility of their effective utilization.

Mechanisms for chemical reactions involved in lignin biodegradation by *Phanerochaete chrysosporium*, T. UMEZAWA: Wood Research, No. **75**, 21 (1988)

Recent studies on "Mechanisms for chemical reactions involved in lignin biodegradation by *P. chrysosporium* were reviewed.

1. Cleavage in propyl side chain by *P. chrysosporium*
2. Aromatic ring cleavage by *P. chrysosporium*
3. Aromatic ring cleavage by lignin peroxidase

Cleavages of aromatic ring and side chain of a (β-O-4)-(β-O-4) lignin substructure model trimer by lignin peroxidase, T. UMEZAWA and T. HIGUCHI: Mokuzai Gakkaishi, **34**, 929 (1988)

Degradation of a lignin substructure model trimer, composed of two β-*O*-4 substructures, by lignin peroxidase of a white-rot basidiomycete (*Phanerochaete chrysosporium* Burds.) was investigated to determine the effect of a propyl side chain of the aromatic ring etherified to the Cβ position on the degradability of β-*O*-4 lignin substructure models by the enzyme. Gas chromatography-mass spectrometric analysis of the degradation products showed that the enzyme catalyzed aromatic ring cleavage as well as side chain cleavages of the trimer. This meant that the propyl side chain did not prevent the aromatic ring cleavage of the β-*O*-4 lignin sub-structure model compounds by the enzyme.

Cleavage of aromatic ring and β-O-4 bond of synthetic lignin (DHP) by lignin peroxidase, T. UMEZAWA and T. HIGUCHI: FEBS Lett., **242**, 325 (1989)

Lignin peroxidase from a white-rot basidiomycete, *Phanerochaete chrysosporium*, catalyzed cleavages of the aromatic ring and the β-*O*-4 bond of a synthetic lignin, a dehydrogenation copolymer (DHP) of coniferyl alcohol and a (β-*O*-4)-(β-β) lignin substructure model trimer.

Degradation of a non-phenolic β-O-4 lignin substructure model compound by *Corioul hirsutus*, K. YOSHIHARA, T. UMEZAWA, T. HIGUCHI and M. NISHIYAMA: Agric. Biol. Chem., **52**, 2345 (1988)

A non-phenolic β-*O*-4 lignin substructure model compound was degraded by *Coriolus hirsutus*, a white rot fungus. The substrate was degraded to give Cα-Cβ cleavage products, β-*O*-4 ether bond cleavage products and aromatic ring cleavage products. The results suggested that the substrate was degraded by lignin peroxidase as in the case of *P. chrysosporium*.

Degradation of a non-phenolic arylglycerol-β-aryl ether by *Streptomyces cyaneus*, W. ZIMMERMANN, T. UMEZAWA, P. BRODA and T. HIGCHI: FEBS Lett.,

239, 5 (1988)

A non-phenolic β-*O*-4 lignin substructure model compound, 1,3-dihydroxy-2-(2-methoxyphenoxy)-1-(4-ethoxy-3-methoxyphenyl)propane, was degraded by *Streptomyces cyaneus* in liquid shaken cultures. 4-Ethoxy-3-methoxybenzoic acid could be identified by TLC and GC/MS as the main product, indicating the cleavage of the Cα-Cβ bond of the aryl glycerol-β-aryl ether. In addition, 4-ethoxy-3-methoxybenzaldehyde and guaiacol were identified in culture extracts as further degradation products.

Aromatic ring cleavage of 4,6-di(tert-butyl)guaiacol, a phenolic lignin model compound, by laccase of *Corious versicolor*, S. KAWAI, T. UMEZAWA, M. SHIMADA and T. HIGUCHI: FEBS Lett., **236**, 309 (1988)

It was found that 2,4-di(*tert*-butyl)-4-(methoxycarbonylmethyl)-2-buten-4-olide (**II**) was formed as an aromatic ring cleavage product of a phenolic lignin model compound, 4,6-di(*tert*-butyl)guaiacol (**I**), by laccase of *Coriolus vesicolor*. Based on isotopic experiments with $^{18}O_2$ and $H_2{}^{18}O$, the mechanism of formation of **II** from **I** is discussed.

Analysis of lignin degradation intermediates by thin-layer chromatography and gas chromatography-mass spectrometry, T. UMEZAWA and T. HIGUCHI: in "Methods in Enzymology, **161**, Biomass Part B, Lignin, Pectin and Chitin" (Eds., W.A. Wood and S.T. Kellogg) Academic Press, Inc., San Diego, pp. 200-210 (1988)

Separation and identification of microbially degraded products of lignin by TLC and GC-MS were described in detail.

Methods used in the chemistry of lignin biodegradation, T. UMEZAWA and T. HIGUCHI: in "Modern Methods of Plant Analysis, New Series Vol. **10**, Plant Fibers" (Eds., H.F. Linskens and J.F. Jackson) Springer-Verlag, Heidelberg, pp. 161-180 (1989)

Chemical methods used in lignin biodegradation were described in detail.

1. Preparation of polymeric lignin
2. Analysis of polymeric lignin degradation products
3. Analysis and identification of low-molecular-weight degradation products
4. Preparation of lignin substructure model compounds
5. Analysis and identification of degradation products of the model compounds

Mechanisms of lignin degradation by lignin peroxidase and laccase of white-rot fungi. T. HIGUCHI, in "Plant Cell Wall Polymers Biogenesis and Biodeg atation, ACS Symposium Series **399**", (Eds., N.G. Lewis and M.G. Paice) Ameri-

can Chemical Society, Washington, D.C., pp. 482-502 (1989)

The main cleavage mechanisms of side-chains and aromatic rings of lignin model compounds and synthetic lignin (DHP) by lignin peroxidase and laccase of white-rot fungi have been elucidated. Tracer studies using ^{2}H-, ^{13}C- and ^{18}O-labeled arylglycerol-β-aryl ethers and diarylpropane-1,3-diols with $^{18}O_2$ and $H_2{}^{18}O$ indicated that side-chains and aromatic rings of these substrates were cleaved via aryl radical cation and phenoxy radical intermediates, in reactions mediated only by lignin peroxidase/H_2O_2 and laccase/O_2.

Aromatic ring cleavage by lignin peroxidase T. UMEZAWA and T. HIGUCHI: in "Plant Cell Wall Polymers: Biogenesis and Beodegradation" ACS Symposium Series **399**, (Eds., N.G. Lewis and M.G. Paice) American Chemical Society, Wishington, D.C., pp. 503-518 (1989)

Aromatic ring cleavages by white-rot fungi and by the enzyme lignin peroxidase are reviewed. Intact cells of white-rot fungi cleave armatic rings of lignin substructure model compounds as well as polymeric lignin. Lignin peroxidase of *Phanerochaete chrysosporium* catalyzes the ring cleavage of β-*O*-4 lignin substructure model compounds and synthetic lignin (DHP). A mechanism for the ring cleavage by the enzyme is described.

Acetylated wood, M. NORIMOTO: Mokuzai Kenkyu Shiryo (Wood Research and Technical Notes), No. 24, 13-30 (1988) (in Japanese)

This review describes recent information on acetylation of wood, properties of acetylated wood, improvement of acoustical properties of wood through acetylation.

Fomarldehyde treatment of materials for wooden musical instruments — Improvement of apparatus and procedure for the treatment, K. MINATO, H. YANO and M. NORIMOTO: Mokuzai Kogyo (Wood Industry), **44**, 115-118 (1989) (in Japanese with English summary)

It has been reported that the acoustic properties of wood vary with vaporous formaldehyde treatment (formalization). However, for the application of this treatment to wooden musical instruments there are many troublesome problems to be solved. We intended to improve the operating procedure to treat the soundboard of string instruments such as violin, mandolin, and guitar. The wood material for these musical instruments is usually valuable and expensive. Therefore, to raise the reproducibility and reliability of the treatment we attempted, 1) designation of a Pyrex glass reaction vessel which endures high temperature and vacuum, 2) preparation of pure formaldehyde vapor, and 3) precise control of the vapor concentrations of formaldehyde and hydrogen chloride catalyst. Though there

remains some problems, e.g. imperfect permeability of reagent into wood and degradation of mechanical properties, the method proposed here was satisfactory one in respects that it made possible to reproduce the reaction conditions and to control the level of treatment. The effect of formalization on acoustic properties of wooden musical instruments will become clear by studying the soundboard prepared by this method.

Wood composites — Present states and direction, 3. Treatments for property enhancement, M. NORIMTO and S. ISHIHARA: J. Soc. Materiels Sci. Japan, **38**, 75-81 (1989) (in Japanese)

Recent information and future direction on the treatments of wood for property enhancement were described.

Periodate oxidation of cellulose by homogeneous reaction, T. MOROOKA, M NORIMOTO and T. YAMADA: J. Applied Polym. Sci., **38**, 849-858 (1989)

Homogeneous periodate oxidation of cellulose was achieved through methylol cellulose. The dissolution of methylol cellulose into aqueous periodate solution was followed by the gradual decomposition of methylol groups at random sites along the methylol cellulose chain. The recovery of glycol hydroxyl groups at the C_2 and C_3 positions on the glucopyranose ring during the above decomposition process caused uniform cleavage of C_2-C_3 bonds by the periodate ion. The oxidation level reached nearly 100% in 10 h. The reduced product of the resulting dialdehyde cellulose, i.e., dialcohol cellulose, resulted in mechanical properties quite different from those of conventional dialcohol cellulose. Examination of the thermal deformation and tensile properties revealed that no notable cellulose degradation occurred during the reaction. Our dialcohol cellulose gave a clear and transparent film with a flexible nature.

Properties of wood-based environment, T. YAMADA: J. Soc. Mat. Sci., **38**, 728 (1989) (in Japanese)

A review of the literature for the effect of physical behavior of wood on the house clima, the subjective sensations and vital phenomena.

Wood-based panels, S. KAWAI: Mokuzai Kogyou (Wood Industry), **43**, 543-548 (1988) (in Japanese)

Changes in wood-based panels industry in Japan for these 15 years are surveyed and the trend of research and development for both new products and production technology in this field is described.

Production technology and the properties of low-density particleboard, S. KAWAI: Mokuzai Keykyu Shiryou (Wood Recuarch and Technical Notes), No. 24 31-44 (1988) (in Japanese)

Low-density (0.3~0.5 g/cm^3) particleboard with superior dimensional stability is required as a substitute panel for plywood. This review discusses the limit for lowering the density of particleboards using isocyanate compound resins and the effects of various factors such as species (density) and configuration of particles, resin content and resin component on the properties of low-density particleboard.

Mechanical properties of boards from different species had linear relationships with the compaction ratio (board density/raw material density) and the lower limit of the compaction ratio was 0.5 for this type of resin. The thickness swelling of the boards was independent of the species of raw material, and increased linearly with increase in the compaction ratio, i.e., low-density (low-compaction) particleboards had better dimensional stability. Linear relationships between mechanical properties and shape factors, based on particle configuration and derived from the fracture mechanics theory, was found. Both mechanical and dimensional properties of boards improved with an increase of resin content, but were generally independent of the formulation of isocyanate compound adhesives such as free-isocyanate group content and functionalyty of crude-MDI.

Thick low-density particleboards were estimated to provide not only high ben -deng stiffness, bearing force, and water resistance, but also excellent thermal insulation, sound inculation, and fire resistance. Such boards were effectively produced with a steam injection press.

Wood composites —Present status and the future trend— II. Element and the properties of wood composites, S. KAWAI and H. SASAKI: Zairyou (Journal of the Society of Materials Science, Japan), **37**, 1470-1476 (1988) (in Japanese)

Wood composites are classified and characterized by the size and the aligment of element. Based on the same viewpoint, factors affecting the mechanical properties and durability of wood composites are explained and recent development and its future course of wood composites is discussed.

Thermal, sound, and fire resistance performance of low-density particleboard, S. KAWAI, H. SASAKI, S. ISHIHARA, A. TAKAHASHI and M. Nakaji: Mokuzai Gakkaishi, **34**, 973-980 (1988) (in Japanese with English summary)

Seraya (*Shorea* spp.) flake-type particles with a density of 0.4 g/cm^3 were pressed into commercial size low-density particleboards (densities 0.30 and 0.40 g/cm^3; thicknesses 30 and 40 mm) using an isocianate compound adhesive. The mechanical

properties and the water resistance of these boards were reported in a previous paper. In this paper, the thermal, sound, and fire resistance performance of the boards are discussed. The results were as follows:

1) The thermal conductivities of low-density particleboards were 0.045 and 0.058 Kcal/mh°C for 0.30 and 0.40 g/cm^3 board densities, respectively, which are almost equivalent to that of insulation fiberboard. The thermal diffusibility of the boards, that is, the thermal conductivity divided by the volumetric specific heat, also was quite small compared with other construction materials. Therefore, thick, low-dinsity particleboards were estimated to provide excellent thermal insulation.

2) The impact-sound level penetrating low-density particleboard flooring caused by both tire-dropping and a tapping machine showed somewhat smaller values than those of plywood and commercial particleboard floors. The transmission loss of air-borne sound for low-density particleboard walls was less in the high-frequency region, and greater in the low-frequency region around 200 Hz than that derived from the theoretical mass law. The sound absorption of low-density particleboards is several times greater than that of commercial particleboards.

3) The five resistance of low-density particleboards was similar to that of commercial particleboards; the time at which the temperature on the unexposed surface the critical temperature of 260°C with either particleboard by the JIS (Japan Industrial Standard) A 1304 standard fire test increased with increases of board surface -density. Boards, 40 mm thick at 0.40 g/cm^3 density, could endure more than 30 minutes of fire exposure.

Molding wood-particle mats I. The effect of the shape and radius of the die on the molding process and board properties, P. YANG, S. KAWAI and H. SASAKI: Mokuzai Gakkaishi, **34**, 989-994 (1988) (in Japanese with English summary)

Lauan particles were used in the production of molded curved boards with different radii of curvatures. The influence of shape and curvature of the dies on the flow of particles during pressing and density distribution within the boards were measured, and the applicability of the method of simulation proposed in the previous paper is discussed. The properties of the molded boards were tested. The results were as follows:

1. The average strain on the curved surfaces of molded boards increased with decreases of the radii oj curved dies.

2. The densities of the curved parts were greater than those of the flat parts when the radii of curvatures of dies were small. Densities of the molded boards increased and became concentrated towards the reentrant corners made between the flat and the curved parts of boards. The maximum density was calculated as 1.0

$\sim$1.1 g/cm^3.

3. Comparing the above experimental results with calculated results, it was concluded that they were similar, and the analytical method proposed in the previous paper would be useful in simulating the molding process of particles.

4. The strength of the reentrant corners made between the flat and curved parts of boards became quite stronger than other parts because of greater compaction of particles.

The manufacturing of particleboard II. Board qualities of sugi and niseakashia, V.C. MALLARI Jr, S. KAWAI, S. HARA, T. SAKUNO, I. FURUKAWA and J. KISHIMOTO: Mokuzai Gakkaishi, **35**, 1-7 (1989)

To determine their utility value, niseakashia (*Robinia pseudocacacia* L.), a lesser-used fast-growing hardwood species, and sugi (*Cryptomeria japonica* D. Don) thinnings, were used as raw materials in the manufacture of particleboard, and their mechanical properties and dimensional stabilities were evaluated.

The mechanical properties of both niseakashia and sugi particleboards increase with increasing board density; at high density, niseakashia boards had similar mechanical property values as those of sugi boards, whereqs the latter had better quality than the former at low density. Niseakashia boards had better dimensional stability than sugi boards. These differences were caused by the differences of the compaction ratios between the niseakashia and sugi boards.

Particleboards bonded with isocyanate resin, regardless of the wood species used, had greatest values in mechanical and dimensional stability properties.

Oriented medium-density fiberboard produced with an electrostatic field I. Effects of fiber shape and configuration on fiber alignment and board properties, S. KAWAI and H. SASAKI: Mokuzai Gakkaishi, **35**, 218-226 (1989) (in Japanese with English summary)

A laboratory scale mat-former with electrostatic orienters positioned below the forming conveyor was developed for aligning wood fibers. Softwoods, lauan, and bagasse fibers, defibrated by different methods, were used as raw materials for producing oriented medium-density fiberboards, and the effects of fiber shape and configuration on fiber alignment and board properties are discussed. These are summarized as:

1) Moduli of rupture (*MOR*) and elasticity (*MOE*) of softwood fiberboards were greater than those of lauan fiberboards. Fibers defibrated with a pressurized double-disk refiner (PDDR) gave greater values of bendeng than those defibrated with a non-pressurized double-disk refiner (DDR).

2) Hammer-milled and refined bagasse fibers had values in board properties

similar to those of lauan fibers. Thus bagasse has a good potential as a non-lignocellulosic raw matierial for fiberboard production.

3) With the electrostatic method, rigid and straight fibers such as bagasse could be aligned better than bent and crimped fibers such as PDDR-refined softwood fibers. The alignment ratio of the *MOR* parallel to the perpendicular direction for bagasse oriented fiberboards was 3.5:1, and that of the *MOE* was 3.8:1, whereas those for PDDR-refined softwood oriented fiberboards were only 1.4:1 for the *MOR* and 1.7:1 for the *MOE* This new mat-former should be modified to improved the alignment of crimped PDDR-refined softwood fibers.

4) Internal bond strength and thickness swelling of boards were not affected significantly by the fiber alignment, fiber species, or defibration methods.

Production of oriented particleboard I. Structure of particle mat formed with oriented particles, Y. YOSHIDA, S. KAWAI, O.R. PULIDO and H. SASAKI: Mokuzai Gakkaishi, 35, 227-233 (1989) (in Japanese with English summary)

A new system for the manufacture of electrostatically oriented particleboards was developed. In this system, the electrodes are set on the reverse side of the forming conveyor. The layered structure of the particle mat formed with this system is discussed. The results are summarized as follows.

1) The particle mat has a multiple-layer construction in which the degree of particle orientation is greatest in the lowest layer. The layers are bormed as particles fall on each surface of the mat layers developed during the mat formation.

2) Factors which have an influence on the relationship between degree of orientation and the height of the particle layers are particle geometry, especially length and length distribution, and the voltage applied between electrodes. The influence of the electrostatic field on the orientation of falling particles was complicated by the structure of the previtusly formed mat which the elctrostatic force lines had to pass through.

3) Two oriented particle mats formed with this system, are piled top to top to form a special mat with better particle orientation on both surface. It is suggusted that the mechanical properties and the anisotropy of the oriented particleboards produced with this system are determined as functions of the particle length distribution, board thickness, and board density.

Particleboard from acetylated albizzia particles I. The effect of acetyl weight gain on mechanical properties and dimensional stability, B. SUBIYANTO, S. YUSUF, S. KAWAI and Y. IMAMURA: Mokuzai Gakkaishi, 35, 412-418 (1989)

The mechanical propertias and dimensional stability of albizzia (*Albizia falcata* Backer) particleboards bonded with isocyanate (IC), urea-melamine formaldehyde

(UMF), and phenol formaldehyde (PF) adhesives are reported. Wafers, prepared with a disc flaker, were hammer milled, resulting in flake-type particles. IC-and PF-bonded particleboards made from acetylated particles of the same species with acetyl weight-gains (WG) expressed as percentages of 5, 12, and 20% also were examined. The results were as follows:

1) Mechanical properties and dimensional stability of albizzia particleboards bonded with IC and PF resins had properties of greater values than those of boards bonded with UMF resin at the same board-density level. The disc-flake type particles had mechanical properties of greater values than those of ring-flake type particles.

2) The mechanical properties and dimensional stability of acetylated particleboards were affected significantly by the acetyl WG depending on the type of adhesive. The values of mechanical properties of IC-bonded boards decreased with increasing acetyl WG whereas no serious effects were obserfed with PF-bonded boards. The dimensional properties of both IC-and PF-bonded boards improved with increasing acetyl WG.

Curing conditions of particleboard adhesives II. Curing of adhesives under high steam pressures of temperatures, B. SUBIYANTO, S. KAWAI, M. TANAHASHI and H. SASAKI: Mokuzai Gakkaishi, **35**, 419-423 (1989)

Curing of particleboard adhesives under high steam pressures or temparatures using a specially designed apparatus is discussed. Urea formaldehyde (UF), urea -melamine formaldehyde (UMF), phenol formaldehyde (PF), phenol-melamine formaldehyde (PMF), and isocyanate (IC) adhesives were used. The target heating -temperature (steam pressures) varied from 120°C (2.1 kg/cm^2) to 200°C (15.0 kg /cm^2), with steam times of 30 to 180 seconds; then after which liquid nitrogen was injected into the cell.

The results obtained were as follows: At high temperature (pressures), the maximum (peak) hardness of cured UF adhesive was observed with short steam-injection time. After this peak, the hardness decreased with increasing steam-injection times for all temperature levels, and the resin finally decomposed to a liquid.

The trends of this phenomenon in UMF and PMF resins were similar to those in UF, and the hardness peak was observed with a longer steam-injection time than that of UF resin.

The hardness of PF adhesive sured with steam injection was quite low compared sith that of PF resin cured under atmospheric pressure.

Isocyanate resins were cured under all steam pressure conditions, and they foamed.

Curing conditions of particleboard adhesive III. Optimum conditions of curing adhesives in steam injection pressing of particleboard, B. SUBIYANTO, S. KAWAI and H. SASAKI: Mokuzai Gakkaishi, **35**, 424–430 (1989)

In steam-injection pressing the effect of the pressing time on the internal bond (IB) strength and the thickness swelling (TS) of particleboards were measured and are discussed. Adhesive resins used were urea formaldehyde (UF), urea-melamine formaldehyde (UMF), phenol formaldehyde (PF), phenol-melamine formaldehyde (PMF), and isocyanate (IC). The steam temperatures, controlled by adjusting the injected-steam pressures, ranged from 120°C (2.1 kgf/cm^2) to 180°C (10.0 kgf/cm^2).

The results were as follows:

The maximum values of IB for UF and UMF bonded boards were observed at lower steam temperatures (about 120°~140°C) and longer pressing-times (120 to 150 seconds). Higher steam-temperatures resulted in poor board properties. Water contained within an adhesive under a high-pressure environment may have accelerated the decomposition of the resin and resulted into the poor board properties. On the other hand, the IBs of PF, PMF, and IC boards were not influenced sensitively by the steam temperature, and greater steam-temperatures seemed to permit shorter pressing-times. All boards produced by steam-injection pressing had better dimensional stabliity than those produced with a conventional hot-platen press.

The trend of the properties of boards produced under high pressure agrees well with that of the adhesives cured under high-pressure reaction-cell conditions reported in the previous paper, but the optimum conditions tend to shift to longer press times.

Carbon-material overlaid particleboard I. Fire endurance and mechanical and physical properties of charcoal-overlaid particleboards S. ISHIHARA and S. KAWAI: Mokuzai Gakkaishi **35**, 234–242 (1989). (in Japanese)

Overlays of charcoal from ubamegashi (*Quercus phylliraeoides* A. Gray) were used in the manufacture of fire-resistive particleboards. The fire endurance of charcoal-overlaid boards was tested by different methods and compared with those of boards without overlays. Charcoal overlays were found to be effective in increasing the fire resistance of boards. Fire endurance of overlaid boards was improved by time delays in temparature rise because of the low level of combustibility of charcoal. Charcoal-overlaid boards also performed well in other fire endurance test cristeria such as absence of ignition and cracks, short after-flame time span, and strength retention.

The moduli of elasticity (MOE) and of rupture (MOR) of boards decreased

slightly due to the charcoal overlay. The average retentions of MOE and MOR in wet-bending of charcoal-overlaid boards were greater than those of the control board.

Internal bond-strength of overlaid boards increased with increase in coarse charcoal overlay but decreased slightly with an increase in fine charcoal overlay.

Charcoal-overlaid particleboards have great dimensional stability. A hysteresis of thickness swelling was rarely observed after immersion in water for 24-hour and 30-day periods, and after immersion in boiling water for a 2-hour pariod. The charcoal-overlaid particleboards enhanced good comparisons with those without overlay.

Carbon-material overlaid paarticleboard II, Fire endurance and physical properties of particleboards overlaid with various types of carbon materials, S. KAWAI, S. ISHIHARA, Y. YOSHIDA and A. TAKAMATSU: Zairyo (Journal of the Society of Materials Science, Japan), **38**, 758-764 (1989) (in Japanese with English summary)

Various types of carbon materials are being used as overlays in the manufac ture of fire resistive particleboards. The fire endurance of carbon materials overlaid particleboards was evaluated by three different methods, and the results were compared with those of boards without any overlay and of non-combusitible commercial boards. The mechanical and dimensional properties of these overlaid particleboards were also examined. The results obtaened were as follows:

1) The fire endurance of overlaid boards was improved both in the time delay in temperature rise at unexposed surface (JIS A 1304) and in burn through when exposed in high velocity flame due to low combustibility of carbon. The creep under fire of overlaid boards showed better performance than those of conventional particleboards and non-combustible commercial structural boards due to high heat -resisting property of carbon. Graphite and charcoal from softwoods saw dust and bark were found to be highly effective as the overlay materials in increasing fire resistance of particleboards.

2) The mechanical properties of overlaid boards were lower than those of the control particleboard. However, they could be improved by reinforcing overlaid boards with glass or carbon fiber clothes, or by veneering.

3) Overlaid boards showed great dimensional stability because of high water resisting property of carbon and low compaction of particles.

Particleboard from acetylated albizzia particles II. Creep under humidity changes, S. TAKINO, M. NORIMOTO, S. KAWAI and H. SASAKI: Mokuzai Gakkaishi, **35**, 625-632 (1989)

Albizzia (*Albizia falcata* Backer) particles were acetylated with acetic anhydride without a catalyst, then hot-pressed into particleboards using three different adhesives: isocyanate (IC), urea-melamine formaldehyde (UMF), and phenol formaldehyde (PF) resins. Creep-tests of these particleboards were conducted under cyclic dry-wet conditions. Static-bending and internal-bond (IB) strength tests were made on the specimens after the creep-test. The results obtained were as follows:

1) Creep-compliance of all the particleboards tested showed a pronounced increase during the first relative humidity (RH) increase. Whereas all first reductions in RH caused a slight increase or decrease in creep-compliance, the second and all later RH increases produced increases in creep-compliance.

2) Among the particleboards made with the three different adhesives, their creep-compliances when compared at the same elapsed time were in the order of UMF-bonded board > PF-bonded board > IC-bonded board.

3) Creep-compliance of the boards decreased with increasing weight-parcent-gain (WPG) because of acetylation. Especially, creep-compliance of acetylated boards with 20 WPG remained almost unchanged after the first RH increase. Creep recovery increased with increases in the WPG of the particles.

4) The effects of acetylation on creep-compliance occurred with smollar WPG in PF-bonded boards sompared with IC-bonded boards.

5) The retention of the modulus of elasticity and the modulus of rupture obtained en a static-bending test on specimens after the creep-test increased with increases in the WPG of the particles. The retention was especially great in IC-bonded boards with 20 WPG and in PF-bonded boards with 12 and 20 WPG. The retention of IB strength was greater in PF-bonded boards than in IC-bonded boards.

Particleboard from acetylated Albizzia particles III. Enhancement of decay resistance, termite resistance, and weathering properties through acetylation, S. Yusuf, M. Takahashi and Y. Imamura: Mokuzai Gakkaishi, **35**, 633 (1989)

Biological resistance and weathering properties of low-density acetylated particleboard made from the perishable wood of the fast-growing Indonesian tree, *Albizzia falcata* Backer, were investigated. Acetylated particles with 5, 12, and 20 WPGs (weight percent gain) were pressed into particleboards (air-dry specific gravity: 0.5) using phenol folmaldehyde and isocyanate resins. Laboratory tests showed that the acetylated boards with the 20 WPG were highly resistant to decay and had satisfactory dimensional stability. Acetylation gave significant enhancement to their termite resistance based on laboratory tests and field exposures in the wet

tropics. However, these low-density acetylated boards are not suitable in environments sustaining a considerable termite hazard. The smaller weight loss and the higher dimensional stability of acetylated boards compared with untreated boards, were revealed after ten weeks of above-ground exposure in the tropical wet season. Our present results suggest that higher acetylation works well to enhance decay resistance and weathering properties of particleboards made from *A. falcata*. However, further improvement is needed to meet termite-resistance requirements.

Effect of acetylation on decay resistance of wood against brown-rot, white-rot and soft-rot fungi, M. TAKAHASHI, Y. IMAMURA and M. TANAHASHI: The Int. Res. Group on Wood Preserv. Document No.: IRG/WP/3540 (1989)

Effect of acetylation on decay resistance of wood was investigated using wood blocks of *Cryptomeria japonica, Pinus densiflora, Albizia falcata* and *Fagus crenata*. Blocks were treated with uncatalyzed acetic anhydride for different lengths of time and exposed to *Tyromyces palustris, Serpula lacrymans, Coriolus versicolor* and unsterilized soil. The action of OH-radical on acetylated wood was also examined using Fenton's reagent. The enhancement of decay resistance by acetylation was revealed clearly for all cases of exposures but varying with fungal and wood species used. For a brown-rot fungus *T. palustris,* the weight loss reached almost nil in all woods at 20 WPG (weight percent gain) of acetylation, after the striking decrease from 10 to 15 WPG. For a white-rot fungus *C. versicolor,* it was counted until 12-15 WPG in the perishable hardwoods used, but not in a softwood *C. japonica,* even at 6 WPG. In cases of another brown-rotter *S. lacrymans* and soil burial, effect of acetylation was intermediate between *T. palustris* and *C. versicolor*. The action of Fenton's reagent on wood was also retarded by acetylation.

Anti-degradation mechanism by acetylation was discussed, from these weight loss - weight gain relationships, and the IR- and ^{13}C-NMR spectral analyses of fungusexposed wood.

Why wood is deteriorated by microorganisms?, M. TAKAHASHI: in "Mokuzai to Kagaku (Wood and Science)", ed. Japan Wood Res. Soc., 80-85, Kaisei-Sha, 150 pp. (1989) (in Japanese)

Biology and biochemistry of wood decay were outlined.

Mushroom and Wood (Kinoko to Mokuzai), M. TAKAHASHI: Biology of Mushroom (Kinoko no Seibutsugaku) Series, No. 6, Tsukiji-Syokan, 130pp. (1989) (in Japanese)

Biology of wood-inhabiting mushrooms, and fungal decomposition of wood and its control were outlined with tables, figures and photographs.

Evaluation of mechanical properties of treated wood-based materials through glue-additive after exposure to fungal attack, Y. IMAMURA and Y. NAKAMURA: Mokuzai Hozon (Wood Preservation), **14**, 178 (1988) (in Japanise)

Plywood, LVLs and Particleboards were prepared by incoporation of fungicides in the glue adhesives, and reductions of their strength properties by fungal attack were characterized. Specimens of low retention of fungicides and with a little weight loss by soil-block decay tests were selected for evaluation of bending strength after exposure to a brown-rot fungus for different periods. Treated specimens held high retention of strength at considerable weight losses at which large strength losses appeared in control specimens. Especially in treated particleboards, it was concluded that the better even distribution of fungicidal forms on the wood particles' surfaces effectively prevent the mycelial developmant in the glue lines, which should cause a significant deterioration of bonding in controls.

Bending-creep tests on acetylated pine and birch particle boards during white and brown-rot fungal attack, Y. IMAMURA, R. M. ROWELL, R. SIMONSON and A. -M. TILLMAN: Paperi ja Puu, **70**, 816 (1988)

Pine and birch particleboards made from acetylated chips at 18.8 and 16.0 percent acetyl weight gains respectively, using melamine-urea folmaldehyde adhesive, were subjected to soil-block tests using *Tyromyces palustris* or *Coriolus versicolor*. While control boards lost between 30 and 55 percent in weight during the 12 week test, acetylated boards lost between 1 and 4 percent. All kinds of boards were also subjected to a bending-creep test under progressive white or brown-rot fungal attack. Inoculated control boards failed within a short pereod when attacked with *T. palustris*, or after a considerable length of time when exposed to *C. versicolor*. For acetylated boards, the brown-rot fungus caused the fracture of specimens, while the white-rot fungus did not cause the specimens to fail. Electron micrographs of all failed surfaces from the brown-rot fungal tests showed that the melamine-urea folmaldehyde resin was attacked by the fungus, eventhough the wood particles themselves were not decayed when they were acetylated.

Detection of termite attack in wood using acoustic emission, Y. FUJII, M. NOGUCHI, Y. IMAMURA and M. TOKORO: The Int. Res. Group on Wood Preserv., Document No. IRG/WP/2331, (1989)

Acoustic emission (AE) is the elastic wave produced by the strain energy released in the process of fracture of a material and propagates through it. The objective of this report is to detect AEs produced by the termite activities and to evaluate the possibility of using an AE monitoring test to nondestructively detect

the termite attack in wood. It was revaled that AEs were detected from the specimens under termite-attack and the rate of AE events increased according to the number of the inhabiting termites. As no AE was detected from the specimens with soldiers only, it was assumed that workers should generate AEs through feeding activities. It was also revealed that the distribution of AE sources corresponded to that of the region attacked by the termites in the specimen.

Dimensional stability, decay resistance, and mechanical properties of veneer-feced low-density particleboards made from acetylated wood, R. M. ROWELL, Y. IMAMURA, S. KAWAI and M. NORIMOTO: Wood and Fiber Science, **21**, 67 (1989)

Veneer-faced low-density particleboards were made using four combinations of control and acetylated veneers and particles. These boards were tested for dimensional stability in both liquid water and water vapor, for decay resistance in standard soil-block tests with *Tyromyces palustris* and *Coriolus versicolor*, for strength losses during during attack by *T. palustris*, and for mechanical strength. Boards made from acetylated veneers and acetylated core particles showed excellent dimensional stability in both liquid water and humidity tests and were resistant to attack by both fungi in an 8-week soil-block test. During the 150-day bending-creep test, the totally acetylated boards showed no strength and weight loss during exposure to *T. palustris*. Modulus of elasticity and modulus of rupture were slightly reduced for totally acetylated boards compared to boards with control veneers and control particles, and internal bond strength was reduced by about 30%. Screw-holding capacity of the totally acetylated boards and boards with control veneers and particles was essentially the same.

Enhancement of biological properties of wood-based materials, Y. IMAMURA: Gohan Report (Plywood Report), No. **11**, 19 (1989) (in Japanese)

Biodegradation of wood-based materials was briefly described, and methods to impart the decay and termite resistance to them were discussed with emphasis on glue-additive treatments. New some concepts to develop high-performance materials from wood products were presented.

Enhanced biological properties of chemically treated wood, Y. IMAMURA: Mokuzai Kogyo (Wood Industry), **44**, 109 (1989) (in Japanese)

The mechanisms of the increased biological resistance of chemically-treated wood were discussed. For chemically modified wood such as acetylated wood, the levels to acheve satisfied decay-resistance were affected by the types of decay fungi as well as wood species and the higher levels of treatment were necessary for control

of brown-rotters. When exposed to termites, inability of symbiotic protozoa to utilize the chemically modified wood was observed as a result of stable chemical bonds in water-accesible regions of the cell wall components. Deposition of incorporated materials in the wood cell walls was considered to afford the practical effects on fungal attack for wood polymer combination or new wood complex with inorganic materials.

Outline of reports of 16th annual meeting of the society for antibacterial and antifungal agents, Japan, Y. IMAMURA: Mokuzai Hozon (Wood Preservation), **46**, 126 (1989) (in Japanese)

Outline of reports on wood preservation, presented at the 16th Annual Meeting of Japanese Society for Antibacterial and Antifungal Agents, which was held in Osaka, May, 1989, is described.

High-performance wood of incombutibility and biological resistance, Y. IMAMURA: Doboku Gakkaishi (J. of Japan Society of Civil Engineers), **74**(8), 30 (1989) (in Japanese)

New principles to impart incombutibility and biological resistance to wood was presented. Notable improvements in resistance against fungal and termite attack through chemical modification or combination with bioactive polymers was briefly described. New method to produce fire-retardative materials through complex with inorganic compounds was also explained.

Characterization of pit structure and some aspects on improvement of wood permeability, Y. IMAMURA: New Lumber Man, No. 72, 1 (1989) (in Japanese)

The structure of pit membranes in bordered pits of softwood was characterized from a view point of wood permeability. The improvement in permeability caused by micro-organism attack or enzyme treatment was also discussed.

Studies of low toxicity anti-sapstain chemicals (3) Laboratory evaluation of some formulations as anti-sapstain and anti-mold agents, K. TSUNODA: Mokuzai Hozon (Wood Preservation), **14**, 215 (1988) (in Japanese with English summary)

Sixteen single chemicals and 6 formulations were tested for their efficacy in controlling molds and sapstaining fungi on wood mainly according to JWPA Standard-II.

When wood specimens were treated with each single chemical at 0.3% a.i. and exposed to *Aspergillus niger* and *Gliocladium virens*, organoiodine compounds (IF-1000,

IPBC) were proved to be effective. Benzimidazoles (Thiabendazole, Mergal HS-100, -BCM) were satisfactorily effective against *G. virens*, whereas other chemicals were relatively less toxic to the test fungus. Chlorinated phenols were ineffective at 0.3%.

Among formulations tested in the present investigation, the followings could protect the treated timber from molds and sapstaining fungi: IF-1000+benzimidazole, TCMTB+MBT and TCMTB+IPBC. Nevertheless, stability tests of treating solutions and field trials are still needed before those candidates come to appear in the market.

Effect of alkyl chain length on the fungicidal efficacy of tertiary amine acetates, K. TSUNODA: J. Antibact. Antifung. Agents, **16**, 515 (1988)

Five tertiary amine acetates with different lengths of alkyl chain were tested for their fungicidal effectiveness according to JIS A 9302. Tetradecyldimethylamine acetate appeared to be the most effective against decay fungi among the chemicals tested, and the retentions which passed the criteria of JIS A 9201 were <2.2 and 2.2~3.2 kg/m^3 against *Tyromyces palustris* (Berk. ex Curt.) Murr. and *Coriolus versicolor* (Linn. ex Fr.) Quél, respectively. The following order of fungicidal efficacy was found among different alkyl chain lengths: $C_{14}=C_{16}=C_{18}>C_{12}>C_{10}$ for *T. palustris* and $C_{14}>C_{16}=C_{18}>C_{12}>C_{10}$ for *C. versicolor*. Comparison of the results obtained for the acetate salts with those for conventional water-borne wood preservative, copper-chrome-arsenate (Celcure K33) suggested that further comparative investigations might be worthy of consideration.

Effect of accelerated ageing on the termiticidal performance of organophosphates. I. Heat exposure, K. TSUNODA, T. YOSHIMURA and K. NISHIMOTO: Mat. u. Org., **23**, 289 (1988)

Organophophates were superior to chlordane in protecting timber from subterranean termites, *Coptotermens formosanus* Shiraki in standardized laboratory tests when sapwood blocks of *Pinus densiflora* Sieb. et Zucc. (1 cm×1 cm×2 cm) were brush-treated at a rate of 110±10 g/m^2. As for unleached wood blocks, chlorpyrifos and phoxim were the best, effective at 0.025–0.05%, and followed by tetrachlorvinphos, pyridaphenthion and chlordane. After wet dry cycles [prescribed in Japan Wood Preserving Association Standard 11 (1)], phoxim performed better than any other chemicals.

Termiticidal activity of organophosphates generally decreased with time of heat exposure at 40°C. The tendency was prominent at lower concentrations. After 12 months' heat exposure, the following concentrations were required for controlling termite attack, producing less than 3% weight loss of treated wood blocks: 0.05–

0.1% for chlorpyrifos; 0.1-0.2% for phoxim, 0.5-1.0% for tetrachlorvinphos and pyridaphenthion; >2.0% for chlordane.

Laboratory evaluation of anti-sapstain formulations, K. TSUNODA: The Int. Res. Group on Wood Preserv. Doc. No. IRG/WP/3510 (1989)

Four formulations were tested for their efficacy in controlling molds and sap-staining fungi on wood according to the Standard-II of Japan Wood Preserving Association (JWPA). Relative efficacy was compared on the basis of visual rating of the fungal growth on the treated and untreated wood surfaces when the wood specimens were exposed to each monoculture of 5 test fungi at 26±2°C and 70~80% RH for 4 weeks.

The results indicated that the formulations containing IF-1000 (p-Chlorophenyl -3-iodopropargyl formal)+TBZ[2-(4-Thiazolyl)benzimidazole], TCMTB [2-(Thiocyanomethylthio) benzothiazole]+MBT (Methylene bis thiocyanate) and TCMTB+IPBC (3-Iodo-2-propynyl butyl carbamate) were superior in anti-sapstaining effectizeness to commercial trichlorophenol-base products. However, the mixture of IF-1000+Mergal HS-100 [2-(Methoxy-carbonyl-amino) benzimidazole-4-n-dodecyl-benzene sulfonic acid] was not satisfactorily effective against *Gliocladium* and *Rhizopus*.

Effect of accelerated ageing on the termiticidal performance of organophosphates. II. Soil burial, K. TSUNODA, T. YOSHIMURA and K. NISHIMOTO: Mat. u. Org., **24**, 17 (1989)

Wood blocks (sapwood of *Pinus densiflora* Sieb. et Zucc.) which had been previously brush-treated with organophosphates at a rate of 110±10 g/m^2 were first subjected to unsterile soil burial for 3, 6 and 12 weeks at 26±2°C and 90±5% R.H. The blocks were then exposed to subterranean termites, *Coptotermes formosanus* Shiraki according to standardized laboratory test method.

Chlorpyrifos performed best and was followed by phoxim. The chemical was effective at 0.4% even after 12 weeks' exposure. Phoxim showed good effectiveness at 0.2% when the period of soil burial was limited to shorter than 6 weeks and still performed well only at 1.0% after 12 weeks' exposure.

Both tetrachlorvinphos and pyridaphenthion disappointingly became ineffective under microbial degradation in the soil.